identification places Γ_{7c} and Γ_{8c} at 3.4 and 3.8 eV, respectively, above the top of the valence band. A second doublet, separated from the first by the energy of the fundamental gap, most likely correlates to transitions from the top of the valence band into the same spin-orbit split set of final states.

This interpretation of some of the multiple and weak structure in the E_0' region on the basis of band population effects will facilitate identification. Our interpretation provides accurate values for energetic position and splitting of higher conduction bands in materials in which band population effects are of importance, such as GaSb and InAs which are under study in this laboratory. Such data provide semiempirical band models with experimental input in a spectral region for which such input is particularly needed.

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Effect of Internal Strains on the Paraelectric Resonance of Li^+ in KCl†

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Paraelectric-resonance data for KCl:Li^+ with a number of crystal orientations at 29.2 GHz are presented. The spectra are in serious disagreement with the predictions of the simple eight-⟨111⟩-dipole model in that two lines appear for certain orientations where only one is expected, and one line appears for other orientations where two are expected. However, these spectra can be explained if internal strains are incorporated into the description.

I. INTRODUCTION

PARAELECTRIC resonance[1,2] may be defined as the process of stimulating electric dipole transitions between energy levels of a paraelectric defect. A paraelectric defect is a crystal imperfection having a permanent electric dipole moment which can exist in one of several equivalent but geometrically different orientations. The particular paraelectric defect produced by the replacement of a K ion in KCl with a Li ion has been studied by several investigators. The theoretical calculations of Quigley and Das[3] and Dienes, Hatcher, Smoluchowski, and Wilson[4] and the experimental findings of Byer and Sack[5] show that the Li ion exists off center of the K-ion vacancy in potential minima with the Li along the ⟨111⟩ crystallographic directions. There is one potential minimum for each of the eight ⟨111⟩ directions, thus, eight different directions along which the electric dipole of the defect may align. This is the basis of the eight-⟨111⟩-dipole model of the KCl:Li^+ system as presented by Bowen, Gomez, and Krumhansl.[6]

Recently, several studies have been made on the paraelectric resonance of KCl:Li^+. Höcherl and Wolf[7] have published spectra obtained at 35 GHz with field parallel to ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions in the crystal. Herendeen and Silsbee[8] have reported paraelectric resonance at 9, 24, and 63 GHz in KCl:Li^+. Their data were for ⟨100⟩ and ⟨110⟩ orientations. In retrospect, it appears that the paraelectric resonance thought to be OH^- in KCl [9] is in fact caused[2,7,10,11] by Li^+, at least for the data obtained above 10 GHz.

The purpose of this paper is to present the paraelectric-resonance spectra obtained for a number of crystal orientations of KCl:Li^+ and to compare the data with the predictions with strains. The angular dependence of the paraelectric resonance in KCl:Li^+ has been little studied. The effect of internal strains on the paraelectric resonance of KCl:Li^+ has been briefly presented by the authors previously[12] and has been discussed in a perturbation sense by Herendeen and Silsbee.[8] The major discrepancies of the simple eight-

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⟨111⟩-dipole model without stress are that only one line is predicted for the ⟨100⟩ orientation whereas two are observed, and that two lines are predicted for certain other orientations, for example, ⟨112⟩, and only one is observed. Extensive numerical calculations including random internal stresses and electric fields indicate that the number of lines observed experimentally can be explained by assuming large internal strains but not by internal electric fields.

II. EXPERIMENTAL TECHNIQUES

The KCl crystals investigated were obtained from Dr. H. C. Wolf and Dr. G. Höcherl of the Technische Hochschule of Stuttgart and from the Harshaw Chemical Co. The KCl received from Stuttgart required little preparation other than cutting to the proper size and orientation since it was grown from a melt doped with LiCl. The Harshaw KCl was classified as of "optical grade" purity, and it was necessary to diffuse[13] in Li before paraelectric resonance could be observed.

The KCl:Li^+ crystals were cut and water polished to the proper size and orientation and then placed, one at a time, in a high-Q rectangular TE_{303}-mode microwave cavity in such a way that the microwave electric field ($\mathcal{E}_{ac}$) and an applied static electric field ($\mathcal{E}$) were parallel to the desired crystal orientation.

The microwave spectrometer was of the homodyne-balanced mixer type designed to operate in the 28–37-GHz frequency range. All measurements to be reported upon here were made at 29.2 GHz, which was the resonant frequency of the fully loaded cavity. Either absorption or dispersion derivatives could be observed independently by proper adjustment of the microwave phase.

III. EXPERIMENTAL RESULTS

Paraelectric-resonance spectra were obtained for eight different orientations from a number of different samples of KCl:Li^+. Each orientation of the KCl:Li^+ samples exhibited one strong line and for some orientations a weaker line at higher field. For each orientation, the value of the electric field at which the line appeared varied somewhat on different days on the same sample or on different samples. The reason for this is not completely understood. The values quoted will be accompanied by "error bars" which are more representative of this variation than of error in the determination of the electric field applied to the sample. The position of the strong lines was easily determined because the maximum of the dispersion derivative closely corresponded to the midpoint between the two extremes of the absorption derivative as expected. The weaker lines, however, presented a more difficult problem, particularly when a line appeared as only slightly more than a hesitation on the shoulder of a stronger line. For these cases, the point of minimum slope was chosen and the line assumed to occur at this value of the electric field.

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TABLE I. Paraelectric-resonance spectra of KCl:Li^+ at 29.2 GHz and 1.3°K.

$\mathcal{E}_{ac}\|\mathcal{E}\|$ crystal orientation	Low-Field line (stronger) (kV/cm)	High-Field line (weaker) (kV/cm)
[100]	6.0±0.5	17.5±1.5
[12,1,0]	5.2±0.4	16.0±1.0
[610]	6.5±0.5	19.0±1.5
[113]	6.8±0.3	16.6±0.5[a]
[112]	7.8±0.5	
[111]	9.5±0.5	
[221]	7.8±0.5	
[110]	7.8±0.9	

[a] Not always present.

Table I presents the data obtained for the different orientations.

IV. COMPARISON OF DATA WITH EIGHT-⟨111⟩-DIPOLE MODEL

The eight-⟨111⟩-dipole model of KCl:Li^+ discussed by Bowen, Gomez, and Krumhansl[6] depicts the electric dipole formed by the off-center Li ion as being displaced along one of the eight ⟨111⟩ directions in the K-ion vacancy. Furthermore, the ion is not isolated in any one potential minimum but can tunnel through the potential barrier to the neighboring minimum, which is the same as saying the dipole can reorient to the nearest ⟨111⟩ direction by tunneling. This is referred to as "cube-edge" tunneling. The tunneling results in a splitting of the energy levels to give a ground manifold of states consisting of a singlet (A_{1g}), triplet (T_{1u}), triplet (T_{2g}), and singlet (A_{2u}) evenly spaced in order of increasing energy. An externally applied electric field leads to a further splitting of some of the energy levels, and a microwave electric field can induce electric dipole transitions between some of the levels.

In Fig. 1, the solid curves show the angular dependence of the isofrequency spectra as predicted by this model. They are frequency-independent provided the ⟨100⟩ minimum is fixed and have the form $1/\cos\theta$, where θ is the angle to a ⟨100⟩ direction. The dots with attached error bars denote the positions of the lines as observed in the laboratory.

Several discrepancies are exhibited upon comparison of the data with the predictions of the eight-⟨111⟩-dipole model with cube-edge tunneling, as can be seen from Fig. 1. The following points may be made about the observations:

(1) The values of the low-field transitions are in fairly good agreement with the theoretical curve. The transitions observed along the three cubic directions are ordered in field as expected with $\epsilon_{[111]} > \epsilon_{[110]} > \epsilon_{[100]}$.

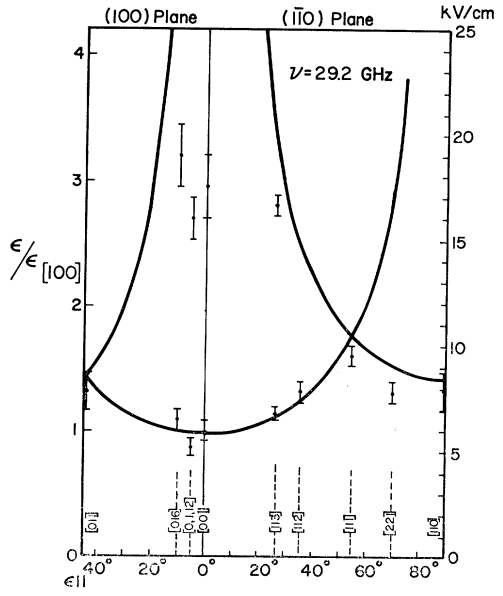

FIG. 1. Angular dependence of isofrequency paraelectric-resonance spectra. The solid curve represents the allowed transitions, and the dots with error bars are the data points.

(2) The high-field lines appearing at and near $\varepsilon \| [100]$ are not predicted.

(3) Two lines were expected for $\varepsilon \| [112]$ with a field ratio of 2:1 and an intensity ratio of 1:2, but only one was observed.

V. EFFECTS OF INTERNAL STRAINS

The eight-⟨111⟩-dipole model as formulated by Bowen, Gomez, and Krumhansl assumes the Li ion to be in an unstressed environment. However, the real crystals on which observations are made are not ideal and so internal strains occur. One might expect the Li^+ paraelectric defect to have an elastic dipole moment as well as an electric dipole moment, and Byer and Sack[5] have shown this to be the case. Thus, the elastic dipole can couple the defect to the internal stress fields and alter the paraelectric-resonance spectra from that predicted by the simpler theory.

Extensive numerical calculations have been made to determine whether the inclusion of internal stresses can explain some of the discrepancies pointed out above. The following steps were taken in calculating the paraelectric-resonance spectra for samples with internal strains. In step 1, a computer program solves the eigenvalue problem for any set of tunneling parameters, electric field, and stress. In step 2, the line positions and intensities are determined for a given fixed frequency. In step 3, the stress is taken as a parameter to obtain an absorption spectrum where the lines are δ functions. To approximate the randomness of the internal stresses, 13 different directions and 9 different magnitudes for a uniaxial stress are assumed. In step 4, these 117 individual spectra are summed up and, in step 5, the δ functions are replaced by Gaussian functions of constant width and an intensity proportional to the line intensities. This process gives a smooth curve similar to that which would be obtained by integration rather than summation in step 4. In step 6, the derivative of the absorption spectrum is taken for direct comparison to the experimental curves. This calculation will be discussed in more detail in a forthcoming paper.[14]

Figure 2 provides a comparison of the experimental and calculated spectrum for the [100] orientation. The experimental trace clearly shows a signal at 17.5 kV/cm in addition to the line at 6.0 kV/cm. The calculated spectrum was based on a 20-GHz zero-field splitting and a dipole moment of 6 D. The Gaussian shape function had a width at half-intensity of 7 kV/cm. As can be seen, the inclusion of internal stresses in the calculation agrees with the experimental spectrum except for details like the asymmetry in the low-field signal which may only require a more detailed calculation. The weak line at 17.5 kV/cm results primarily from the $1E$-$2A_2$ and the $1B_2$-$2E$ transitions which are forbidden in zero stress but weakly allowed for the stress distribution used.[14] The intense line at 6 kV/cm is the line allowed even for no strain.

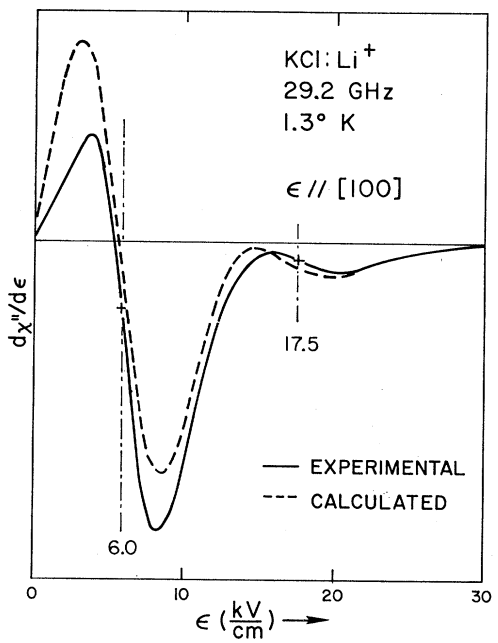

FIG. 2. Comparison of experimental and calculated spectrum for the $\varepsilon \| [100]$ orientation.

[14] B. Dischler (unpublished). The calculated spectra shown in Figs. 2 and 3 were obtained for a uniform stress distribution. The minimum was zero and the maximum corresponded to a splitting of 49 GHz if the stress is along a ⟨110⟩ direction. Put another way, the strain varied from zero to about 2×10^{-4}. It is not yet clear how much these assumptions may be modified and still get agreement with the data.

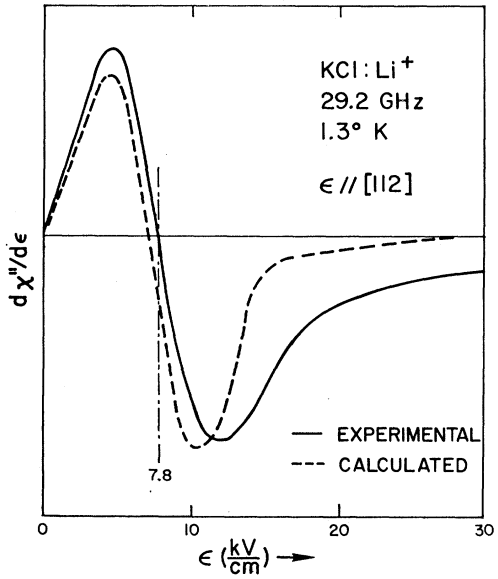

FIG. 3. Comparison of experimental and calculated spectrum for the $\varepsilon \| [112]$ orientation.

Figure 3 compares the experimental scan to the calculated curve for the [112] orientation. The calculated spectrum was obtained as described above except that only four different directions of internal stress were taken. This is further yet from the consideration of a completely random internal stress field than the [100] calculation, but even so, the one signal obtained experimentally can be explained by stress effects. In this case, the effect of the strains is to cause the two lines allowed with no stress to merge into a single line.

The calculations displayed in Figs. 2 and 3 were actually made using tunneling parameters slightly different from cube-edge tunneling. However, no qualitative difference in the spectra should result from this choice.

VI. CONCLUSIONS

Many features of the KCl:Li^+ system may be understood by assuming the eight-⟨111⟩-dipole model with no internal strains. However, the additional high-field signal in the [100] spectrum and the missing high-field line in the [112] spectrum cannot be explained on this basis, even allowing for an arbitrary set of tunneling parameters. Therefore, the effects of internal electric fields and internal stresses which may occur at random at the site of the Li ion have been investigated. Internal electric fields cause essentially a uniform broadening of the allowed lines, but do not explain the [100] and [112] spectra. The assumption of internal strains gives close agreement between calculated and observed spectra. The effect of the internal strain is that it splits allowed lines and causes some formerly forbidden transitions to become observable, thus, leading in some cases to extra experimental signals and in other cases to a consolidation of two resolved lines into one broad signal Herendeen and Silsbee[8] also explain weak lines in their spectra in the same way.

Internal strains or electric fields have been suggested as the explanation for the large linewidth observed in paraelectric resonance[15,9] and for the form of the specific-heat anamoly of paraelectrics.[16,17] Our studies suggest an even more dramatic influence on paraelectric resonance. It appears likely that any measurements which are at all sensitive to the zero-applied-field energies and eigenfunctions will be effected by internal strains.

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